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Citation: *J. Appl. Phys.* **59**, 3607 (1986); doi: 10.1063/1.336792

View online: <http://dx.doi.org/10.1063/1.336792>

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Oxygen doping in close-spaced-sublimed CdTe thin films for photovoltaic cells

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(Received 2 October 1985; accepted for publication 16 January 1986)

Efficient CdTe/CdS thin film solar cells have been the recent focus, in which the CdTe layers were reported by close-spaced sublimation, and oxygen was used to control the *p*-type conductivity of the deposited films. Both the fundamental gap and the impurity level were determined by the wavelength modulation reflectance spectroscopy, which demonstrates that while oxygen atoms have an ionization energy of about 0.1 eV, they do not behave as a simple shallow acceptor. This finding is supported by the electrical characterization. The oxygen concentration incorporated in the CdTe thin films were found to be in the range of 10^{19} – 10^{20} cm⁻³ by the IR measurements, while a carrier concentration between 10^{10} and 10^{12} cm⁻³ was obtained by Hall measurements.

Recently, stable CdTe/CdS thin-film solar cells with efficiency 10.5% and 12.5% have been reported.^{1,2} To date, this is the highest efficiency reported by any thin film solar cell system. The two most prominent deposition techniques are close-spaced sublimation (CSS)¹ and screen printing.² The behavior of dopants in CdTe has been examined by Kroger and De Nobel and others.^{3–6} The *n*-type material is easy to dope with Zn, In, Al, or I and good electrical activity of the dopant is obtained in both crystals and films. The *p*-CdTe is more difficult to produce. Commonly used dopants are P, Au, As, and Li. It is difficult to obtain material with concentration higher than 6×10^{16} cm⁻³. For doping levels above this, the electrical activity of the dopant drops sharply and the hole mobility is reduced. The difficulty in doping *p*-CdTe stems from both strong compensation effects and low solubility of the usual dopant species.⁷

The most interesting work of film preparation was that of Tyan *et al.*,¹ in which both CdTe and CdS thin films were prepared by CSS technique, and oxygen was unusually used as an efficient dopant for *p*-CdTe. However, no detailed analysis of CdTe thin films deposited by CSS has been reported, and the role of oxygen in CdTe has yet to be determined. Therefore, understanding of oxygen doping in CdTe is an important problem, which might help in the cell further development.

In this work, CdTe thin films have been deposited by CSS, and subjected to electrical and optical characterizations such as wavelength modulation reflectance (WMR) spectroscopy in the spectral range between 1.2 and 3.5 eV at room temperature. Some of our WMR results are checked with EER (electrolyte electroreflectance) measurements. The oxygen content in the films was measured by IR spectroscopy.

The CdTe layers were deposited on glass substrates by CSS. The apparatus we used is similar to the one described by Tyan *et al.*¹ The deposition was carried out at a pressure 1–2 Torr and the temperature was held at 500–600 °C. The WMR and EER spectra at room temperature were mea-

sured by using standard phase-sensitive techniques as described elsewhere.⁸ The oxygen content of CdTe thin films was determined by measuring the infrared absorption caused by the local vibration mode of the oxygen. The method uses the relationship between the oxygen concentration and the absorption coefficient of the 450–510 cm⁻¹ infrared absorption band associated with oxygen in CdTe.⁹

Figure 1 shows typical WMR spectra of CdTe thin films with and without oxygen doping. An absorption dip is clearly seen near 1.5 eV. The energy gap can be computed from the derivative spectra of the real and imaginary parts of the

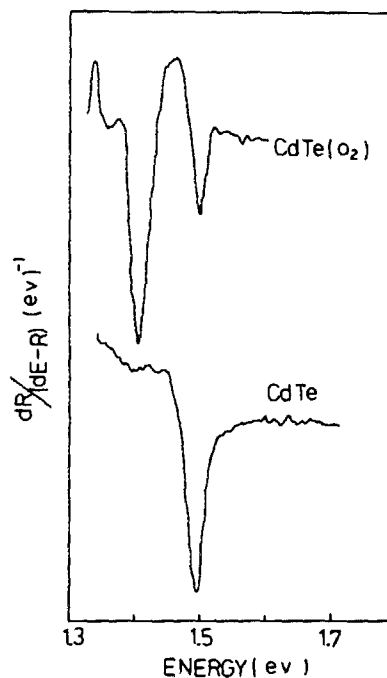


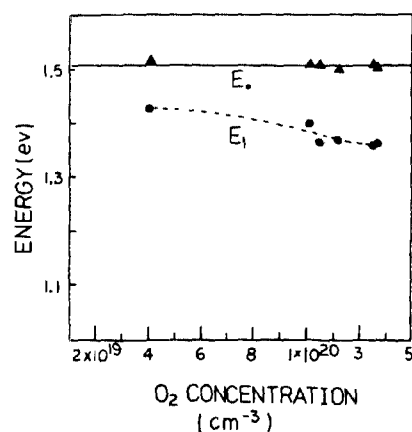
FIG. 1. Typical WMR spectrum of CdTe thin film with and without oxygen doping.

TABLE I. Optical characterization of CdTe thin films and single crystals.

Sample no.	Type of sample	Oxygen concentration (10^{19} cm^{-3})	Experiment	E_0 (eV)	E_i (eV)
V-CTF-12	Thin film	...	WMR	1.493	...
V-CTF-17	Thin film	4.05	WMR	1.515	1.431
V-CTF-15	Thin film	11.8	WMR	1.503	1.404
V-CTF-5	Thin film	14.8	WMR	1.508	1.362
V-CTF-18	Thin film	21.9	WMR	1.500	1.371
V-CTF-10	Thin film	35.3	WMR	1.509	1.359
V-CTF-9	Thin film	36.2	WMR	1.506	1.367
V-CTF-19	Thin film	...	WMR	1.505	...
V-CTF-1	Single crystal	...	WMR	1.503	...
V-CTF-1	Single crystal	...	EER	1.491	...
Cardona ¹⁴	Single crystal	...	EER	1.490	...

dielectric constant ($d\epsilon_1/dE$ and $d\epsilon_2/dE$) using Kramers-Kronig analysis. These computations show that the energy gap is exactly at the position of the absorption dip. The absorption at 1.5 eV is associated with the fundamental $E_0(\Gamma_{8V} \rightarrow \Gamma_{6C})$ transition of the CdTe. For the purpose of comparison, we measured the energy gap of the CdTe single crystals, grown in our laboratory by traveling heater method using the same methods. All the CdTe thin films including oxygen-doped and undoped exhibited a fundamental energy gap at 1.50 ± 0.01 eV as shown in Table I. This energy gap agrees with our and Cardona's results of single crystals.¹⁰

With oxygen doped layers, another dip in the WMR spectra is found near 1.4 eV. This secondary absorption, which was distinctly found to arise from the oxygen incorporated in the CdTe thin films, is interpreted as the impurity transition from an acceptor level to Γ_{6C} . This acceptor level is separated from Γ_{8V} by a difference of nearly 0.1 eV. It was found that the impurity energy level is related to the oxygen concentration determined by IR spectroscopy. The oxygen concentration was estimated between 10^{19} – 10^{20} cm^{-3} , which is higher than previously reported for any other species incorporated in CdTe. The results of WMR and IR are summarized in Table I and Fig. 2.

FIG. 2. The relationship between the fundamental (E_0) and impurity (E_i) transitions and the oxygen concentration in the CdTe thin films.

marized in Table I and Fig. 2.

The doping effect of oxygen in semiconductors is rather complicated. In the case of Si, oxygen has three effects: donor formation, yield strength improvement, and defect generation by oxygen precipitation.¹¹ In the case of GaAs, oxygen atoms behave as deep donors in melt grown crystal,¹² and O^+ -implanted crystals, while as shallow donors in LPE grown crystals.¹³ In the case of InP, the oxygen atoms did not behave as shallow nor deep impurities in the crystal.¹⁴

In the case of CdTe thin films, oxygen atoms behave as efficient acceptors for photovoltaic cells.¹ According to our WMR measurements, the ionization energy of oxygen was determined to be about 0.1 eV, and the oxygen concentration was estimated to be 10^{19} – 10^{20} cm^{-3} from our IR measurements. This is in contrast to the Cu doping in CdTe, which exhibited a room-temperature hole concentration as high as $1 \times 10^{18} \text{ cm}^{-3}$, the highest so far reported for p -type CdTe.¹⁵

In the CdTe, both foreign atoms and native point defects

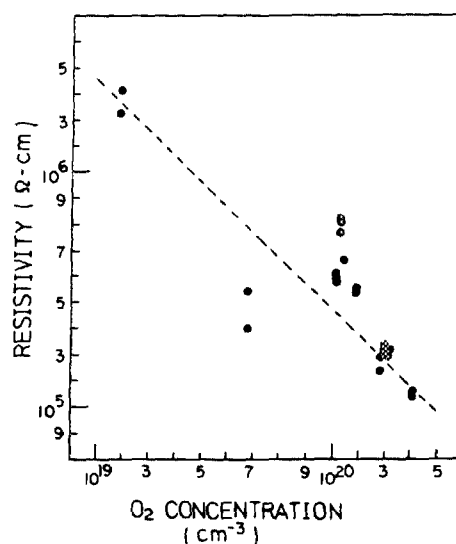


FIG. 3. The relationship between the electrical resistivities and the oxygen concentration in the CdTe thin films.

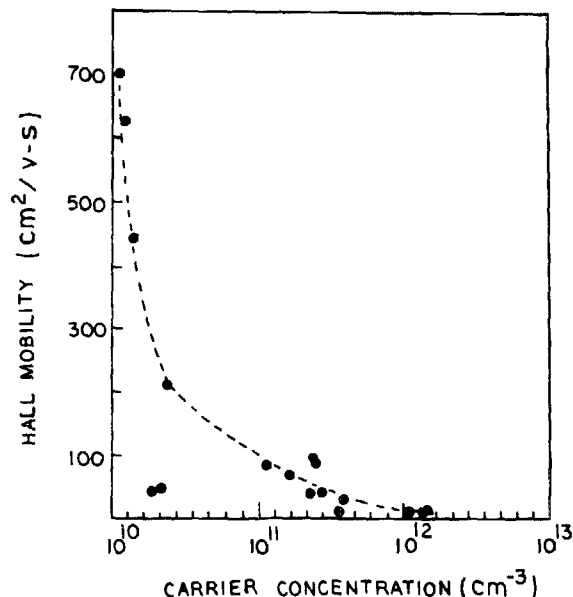


FIG. 4. The relationship between the Hall mobilities and the carrier concentration of CdTe thin films as determined by the Van der Pauw/Hall measurements.

of Frenkel-type (V_{Cd}, Cd_i) and Schottky-type (V_{Cd}, V_{Te}), determine the electrical properties of CdTe. The concentrations of the dopant atoms and defects are not independent on each other. One reasonable explanation of oxygen doping by Chapnin¹⁶ is the formation of acceptor complexes consisting of a structure defect (probably a cadmium vacancy) and an impurity (for example, oxygen). Similar complexes such as ($V_{Cd}-Cl$) and ($V_{Cd}-In$) were also reported and their hole ionization energy was estimated to be 0.14 and 0.17 eV, respectively.^{17,18} It is noted that the ionization energy for oxygen in CdTe thin films increases slightly with increasing oxygen concentration. This is different than reported for Ge and Si.¹⁹⁻²¹ Also, no band-gap narrowing was detected in our heavily doped CdTe thin films. It appears that oxygen complexes do not necessarily behave like simple donor or acceptor impurities.

Figure 3 shows the electrical resistivities of CdTe thin films as a function of oxygen concentration, as determined by IR spectroscopy. Figure 4 shows the corresponding Hall mobilities as a function of carrier concentrations, as determined from the Hall measurements. From Fig. 3, it is obvious that although there is some reduction in resistivity when oxygen is incorporated into the CdTe thin films, the values are still too high (i.e., not less than $10^5 \Omega \text{ cm}$). This supports our previous finding that oxygen does not seem to behave as a simple acceptor with an ionization energy of about 0.1 eV. For shallow acceptors in CdTe, the ionization energy should usually be less than 0.05 eV.²²

Furthermore, the effective carrier concentration determined from the data shown in Fig. 4 is less than $3 \times 10^{12} \text{ cm}^{-3}$. This provides evidence that oxygen atoms in CdTe do not exhibit simple shallow acceptor behavior, even though a

large quantity of oxygen ($10^{19}-10^{20} \text{ cm}^{-3}$) was incorporated in the CdTe thin films. Whether oxygen atoms behave as isoelectronic traps in view of the slight reduction in resistivities by their incorporation has yet to be verified.

Since the compensation process in oxygen doped CdTe is more complex than previously thought, additional experiments such as ESR, and the measurement of the effect of various deformations on the luminescence spectra are required before the actual structure of the oxygen centers can be determined.

In this communication we have reported experimental results on the incorporation of oxygen during the deposition of the CdTe layer by CSS. Oxygen was not known to be a *p*-type dopant to CdTe. Our work clearly establishes that oxygen atoms have an ionization energy of 0.1 eV but do not behave as shallow acceptors. The oxygen content from the IR measurements was found to be unusually high ($10^{19}-10^{20} \text{ cm}^{-3}$), but this did not result in band-gap narrowing. Also, the increase in oxygen concentration did not decrease the impurity ionization energy. Both results do not follow the conventional theory of simple impurity doping. Therefore, the creation of complexes based on cadmium vacancy and oxygen ions which might give rise to an isoelectronic trap center has been proposed. Further investigations are necessitated before definite conclusions can be drawn.

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